

The University of Chicago

THE ENERGY OF IMMERSION OF POWDERS

A DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1930

By
ROY DAHLSTROM

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The Energy of Immersion of Powders

The energy relations at liquid-solid interfaces are practically unknown. It is probable that a study of these relations would lead to a better understanding of many of the problems of colloid chemistry. For example, the stability of paints, lacquers, and of colloidal suspensions might be studied through a more complete knowledge of these energy relations. At the present time there is no method by which the free energy of immersion of a solid may be measured; neither can the free surface energy of a solid be determined; therefore, it is impossible to calculate the former. Some information concerning these energy relations at solid-liquid interfaces can be gained from a study of the total energy of immersion, which is a measure of the "wettability" of a solid. A method for measuring this quantity has been developed and is presented in this paper together with some of the results obtained by it.

Measurements of heats of immersion have been reported in the literature, but most of these have been done on porous solids such as charcoal and silica gel. No direct measurement of the area of the solid is possible and any apparent area determined by indirect means is of doubtful significance. Other measurements yield data for the energy of immersion of a solid whose surface is already covered by a

film of liquid. The results discussed in this paper are for crystalline powders with clean surfaces. The surface area for two of these powders was obtained by a new adsorption method.

The total energy of immersion of a solid in a liquid is given by the change in surface energy when the solid with a clean surface is immersed in a liquid. Since all of the energy appears as heat we may write

$$Q = E_1 - E_{s,l}$$

where Q is the heat evolved, E_1 is the energy of immersion, E_s the surface energy of the solid, and $E_{s,l}$ the interfacial energy at the solid-liquid boundary. All that is necessary for the measurement of the total energy of immersion is a calorimeter so designed as to determine the minute quantity of heat evolved.

Apparatus.

The calorimeter (Figure 1) was a 500 c.c. Pyrex Dewar vessel, silvered on the side exposed to the vacuum. For each experiment 350 c.c. of liquid were put into this vessel. The powder in a sealed, evacuated tube was immersed in a thermostat at 25 ± 0.002 C. for 24 hours before the experiment was started. The calorimeter was opened by removing the cap on the tube I and the powder was poured through the opening into the liquid.

The rise in temperature was measured by means of a

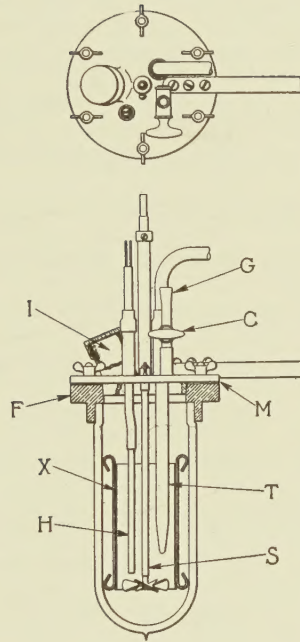


Figure 1—Calorimeter for Determination of Energy
of Immersion of a Powder.

36-junction thermo-element, T, made of No. 26 constantan wire and No. 32 copper wire, according to the method of W. P. White¹. The "constant end" of the thermo-element was immersed in a second Dewar vessel filled with water at the temperature of the thermostat. This afforded a lag which smoothed out any fluctuations in the thermostat temperature. The potential between the leads of the thermo-element was determined by means of a double combination White potentiometer with a range of 10,000 microvolts. A Leeds and Northrup high sensitivity galvanometer was used with the scale at a distance of four meters. Readings to 0.00001⁰ C. were obtained and these seemed accurate to 0.00005⁰ C.

A tube of nichrome, X, was used to increase the effect of the stirrer, S. The heat capacity of the calorimeter and its contents was determined by calculating the heat developed by a constant, known current of electricity, passed through the heater, H. The heating element was of No. 26 constantan wire approximately 30 ohms in resistance. Two storage cells furnished the energy.

Several stirring devices were tried in preliminary experiments, carried out in an unsilvered calorimeter in order that the stirring might be observed. A single, 3-blade propeller, 4 cm. in diameter, placed near the lower end of the tube, X, was found to be most satisfactory. 35 to 40 grams of powder was stirred efficiently at rates varying from

1 W. P. White, J. Am. Chem. Soc. 36, 2292, (1914).

400 to 600 revolutions per minute, depending upon the nature of the liquid and powder. All metal parts were gold plated for use with corrosive liquids.

Procedure

About 35 grams of the powder was put in a Pyrex tube and heated in a vacuum for 24 hours. The vacuum was produced by a mercury condensation pump, supported by an oil pump. The temperature was kept high, but not so high as to change the size of the crystals. With titanic oxide this temperature was 400^o C.

About 350 cc. of water or of the very dry organic liquid was put in the specially dried calorimeter (Figure 1), which was immersed in the water of a thermostat, but with the cap of I above the surface. The cool liquid was brought to the temperature of the thermostat by passing a current of electricity through the heater, H. An hour later the potential of the thermo-element, T, was determined, and the stirrer was started (a, Figure 2). The stirring gave a rise of temperature along the line ab. After about 10 minutes the powder was quickly poured into the liquid and this caused the temperature to rise rapidly. Practically all the heat of immersion was given off in less than 2 minutes. After this the stirring caused the temperature to rise linearly along the line cd. After about 10 minutes more an electrical current was passed through the heater until the resultant increase

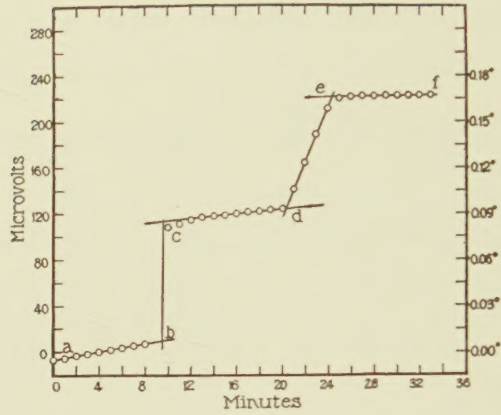


Figure 2—Heating Curve. bc heat of immersion;
de heat produced by heater.

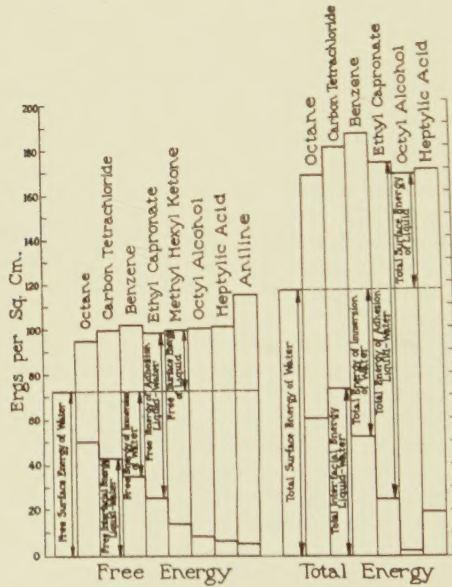


Figure 3—Energy Relations of Water.

of temperature was approximately as great as that given earlier by the powder. The current was then turned off and the temperature rose slowly, as a result of stirring, along the straight line ef. The electrical heating was started and stopped by means of a relay actuated by the pendulum of a clock. The slopes of the rating periods in figure 2 are typical for cases where water is the liquid.

The high heat of immersion of solids in water makes it essential to dry carefully, not only the organic liquids, but also the calorimeter and the other vessels in which they are stored, and to avoid all contact with the atmosphere. Benzene was dried by means of sodium wire. For a period of about two weeks fresh charges of the wire were introduced at intervals of a few days. Then the benzene was transferred, out of contact with the atmosphere, to an all-glass, closed distilling apparatus where, before being distilled, it was refluxed over sodium for several hours. After distillation the benzene was cooled slightly below 25 °C. and introduced into the calorimeter which had been drying for two days; the air used for this had been passed through sulphuric acid, next through a five-foot tube containing phosphorous pentoxide, and then through the calorimeter. The distilling apparatus was dried by the same method. Alcohols and esters were dried by means of metallic calcium. It was found that butyl alcohol could be dried sufficiently by refluxing over calcium for an hour. About 20 percent of the alcohol was lost. Acetone was dried over sodium sulphate at -80 °C.

Calcium chloride was used to dry butyric acid. The magnitude of the effect of moisture decreased with the increasing polarity of the liquid as will be shown by the data presented.

When a non-polar liquid such as benzene was under investigation the sealed tubes containing the powder were broken in an atmosphere of the dried liquid in order that moisture might be further excluded.

Calculation of Results; Precision

The vertical distance de (Figure 2) was taken at the midpoint of the heating period. This represents the change in microvolts due to the introduction of a known amount of heat, Q_2 . The powder was introduced one minute after taking the final reading of the first rating period. On the basis of repeated trials, the energy was assumed to be completely liberated thirty seconds later. The vertical distance, bc , was taken at this point as the change in microvolts due to the energy of immersion, Q_1 which is given by the relation

$$Q = Q_1 \frac{bc}{de}$$

This graphic method was compared with the more exact but time-consuming methods as described by White¹ and found to agree well within the experimental error.

The ratio of results obtained with two samples of titanic oxide, having different surface areas, agreed with

1 W. P. White, The Modern Calorimeter. The Chemical Catalog Co., 1928.

the corresponding ratio from direct adsorption measurements by Gans and with results obtained by Gans and Brooks¹ from measurements of pressure changes upon adsorption of a vapor. In general, the degree of precision was highest with water and lowest with benzene. This was not due so much to the relative magnitudes of the quantities measured as to the difficulty in keeping moisture out of the less polar liquids.

Results and Discussion

The total energies of immersion for four oxides and for barium sulphate are given in table 1. The differences in values for any single liquid are not very great in any case, but this is largely accidental since the heat of immersion per gram is highly dependent upon the fineness of the material.

Table 1. Total Energy of Immersion of Powders in Liquids.

Liquid	Titanic oxide	Stannic oxide	Zinc oxide	Silica	Barium sulphate
	calories per gram of powder				
Water	1.15	0.685	1.18	0.803	0.897
Butyric acid	0.883			0.750	
Ethyl acetate	0.800	0.506	0.737	0.623	0.650
Butyl alcohol	0.769	0.531	0.690	0.550	0.685
Acetone	0.667				
Carbon tetra-chloride	0.526	0.325			
Benzene	0.390	0.220	0.300	0.205	0.230

1 Gans and Brooks, Unpublished

Table 2 shows more clearly the relative effects of various liquids, since the values for water have been set equal to unity. It should be noted that there is a striking uniformity in the horizontal columns. The relative values for zinc oxide, silica, and barium sulphate in benzene are practically identical while those for titanitic oxide and stannic oxide are not very different. Butyl alcohol also gives approximately the same value for all of the different substances.

Table 2. Total Energy of Immersion of Powders in Liquids.

Liquid	Titanic oxide	Stannic oxide	Zinc oxide	Silica	Barium sulphate
	Relative values, water = 1.				
Water	1.00	1.00	1.00	1.00	1.00
Butyric acid	0.768			0.934	
Ethyl acetate	0.696	0.739	0.625	0.776	0.725
Butyl alcohol	0.668	0.775	0.585	0.685	0.764
Acetone	0.580				
Carbon tetrachloride	0.457	0.474			
Benzene	0.339	0.321	0.254	0.255	0.256

Greater differences are found with butyric acid, but this is to be expected since it acts chemically on zinc oxide, so that the energy of immersion cannot be determined by this method. Without regard for those cases which are evidently

influenced by reactions, the absence of any specificity for the oxides and barium sulphate indicates that adsorption phenomena should be considered physical rather than chemical in nature. The tremendous effect of impurities, present only in traces, makes it seem likely that this evidence would be greatly strengthened if greater purity of materials could be attained.

The heat of immersion of a powder in benzene is only one-quarter to one-third as high as with water, but with butyric acid it is almost as high as with water; the values for ethyl acetate are slightly lower and for butyl alcohol, still lower. In general, it may be said that the energy of immersion increases with the polarity of the group at the end of the organic molecule. The high position of water in table 1 is due in part to the smaller area occupied by water molecules in comparison with the more complex organic molecules.

Similar conclusions concerning change of energy of immersion with the polar character of the molecules may be drawn from table 3. The solutions of the different linseed oils have been made so dilute that the energy of immersion of titanic oxide in the solutions is to some extent a measure of the amount of oxidized material present. The results agree with what is known concerning the relative degrees of oxidation of these linseed oils.

Table 3. The Total Energy of Immersion of Titanic Oxide in Solutions of Linseed Oils.

Liquid	Calories per gram
0.1% blown linseed oil + 99.9% benzene	0.780
0.85% boiled linseed oil + 99.15% benzene	0.751
0.1% kettle-bodied linseed oil + 99.9% benzene	0.740
0.1% boiled linseed oil + 99.9% benzene	0.707
0.06% raw linseed oil + 99.94% benzene	0.630

It is interesting to note that the presence of 0.1% of the blown oil increased the energy of immersion of titanic oxide in benzene by 100%.

If table 1 could be expressed in terms of the energy per square centimeter of solid surface, the results would be more valuable. An estimate of the area for titanic oxide was made by E. J. Dunn¹ from microscopic and ultra-microscopic investigations. He calculated from the diameters of the crystals as determined microscopically, that the area of the surface of a set of spheres with the diameters determined is 12.6 meters per gram of powder, but considered that the ultra-microscopic particles would increase this area by an equal amount. The total apparent area was determined by Gans^{by}

1 E. J. Dunn, Ind. and Eng. Chem., Analytical Edition, Vol. 2, p. 59.

the adsorption of oleic acid from solutions in benzene. It was assumed for these calculations that the average area occupied by an oleic acid molecule on the surface of a titanic oxide crystal is the same as the area occupied in films on water. This area is about 20 sq. Å per molecule. Thus Adam¹ finds the mean area of such molecules to be about 20.5 sq. Å at zero compression, while Harkins and Morgan² obtained 19.7 sq. Å with films on water. The corresponding area for such molecules in films on glass was found by Müller³ to be 18.5 sq. Å.

Table 4 gives the total energy of immersion per square centimeter of surface for titanic oxide and stannic oxide on the basis of the areas determined by Gans.

Table 4. Total Energy of Immersion and Energy of Adhesion for Titanic Oxide and Stannic Oxide on the Basis of Areas Determined from Direct Adsorption Measurements.

Liquid	Titanic Oxide I		Stannic Oxide	
	Total energy of immersion	Energy of adhesion	Total energy of immersion	Energy of adhesion
	ergs per sq. cm.		ergs per sq. cm.	
Water	1300	1417	2260	2377
Butyric acid	1000	1055	1290	1345
Ethyl acetate	906	967	1660	1721
Butyl alcohol	870	919	1750	1799
Carbon tetra-chloride	595	658	1230	1293
Benzene	440	509	725	794
	Titanic Oxide II			
Water	1180	1297		
Ethyl acetate	887	948		

1 N. K. Adam, Proc. Roy. Soc., 101A, 452, (1922)

2 Harkins and Morgan, Proc. Nat. Acad. Sci. 11, 637, (1925)

3 Müller, Proc. Roy. Soc. 114, 542, (1927)

The energy of adhesion, which increases with the energy of immersion, is also given. The energy of adhesion is the amount of energy per square centimeter of area which must be applied in order to separate the liquid from the powder, or it is the amount of energy liberated when one square centimeter of the solid is wet by one square centimeter of the surface of the liquid. The relation between the energy of immersion, h_i , and that of adhesion, h_a , is

$$h = h_i + h_a$$

in which h_i is the total surface energy of the liquid.

The energy of immersion of any of these powders is relatively low in a non-polar liquid, such as hexane, octane, or benzene, and is very high in water, which is a highly polar liquid. In general, for the organic liquids which have been used, the energy of immersion of any of these powders gives the same order of the values as the energy of immersion of water in the same liquids. In this sense the surface relations of solids are very similar to those of water. The values for water are given in table 5, in which the data under consideration are those for the immersion of water in the liquid.

Table 5. Free and Total Energy of Immersion of Water in Organic Liquids, and of Organic Liquids in Water.

Liquid	Water in liquid		Liquid in water	
	Free	Total	Free	Total
	ergs per sq. cm.		ergs per sq. cm.	
Heptylic acid	65.2	97.9	20.6	33.4
n-Octyl alcohol	64.2	120.0	19.0	53.5
Ethyl capronate	51.5	92.9	4.6	31.0
Carbon tetrachloride	27.7	43.2	-18.3	-11.0
Ethylene bromide	35.6	48.3	1.6	9.7
Benzene	37.8	65.4	- 6.1	17.3
Hexane	21.8	58.8	-32.5	- 8.8
Octane	21.9	57.2	-29.0	- 9.7

The last two columns of this table give the energy for the immersion of the liquid in water. The analogous case for titanic oxide would be to immerse droplets of water in crystals of the solid oxide. In such a case it is possible to have heat absorbed, instead of liberated, but it is evident that this case cannot be tested.

The relation of energy of immersion to surface and interfacial energy and to the energy of adhesion is shown graphically in Figure 3, in which the free energy values are shown on the left, and the total energy values on the right. Almost the only difference between the two is that the values for the total energy are much larger than those for the free energy. The horizontal dashed lines give the free or total surface energy of water. The value of the interfacial free or total energy is given by the vertical distance from the x-axis up to the first heavy horizontal lines. The value of the free or total energy of immersion of water in the organic liquid is given by the distance from these lines up to the horizontal line. The free or total energy of adhesion is equal to the distance from the same heavy horizontal lines up to the highest heavy horizontal lines. The free or total surface energy of the organic liquid is given by the distance from the dashed line to the upper heavy horizontal lines.

If the horizontal dotted lines are now supposed to represent the free or total surface energy of a solid instead of water, the diagram shows the general relations re-

markably well. The principal difference is that the values for the energy scale on the x-axis up to the dashed line should be made several times larger, but those above the dashed line should remain the same as those given in the figure. That is, the true relations are given by a vertical stretching of that part of the diagram which lies below the horizontal dashed lines.

As has already been indicated, the presence of small quantities of polar liquids produces a great increase in the energy of immersion of a powder in a non-polar liquid. This makes it necessary to use extreme care in purifying non-polar liquids such as benzene and hexane for heat of immersion measurements. Figures 4 and 5 show this influence more clearly.

Solutions for heat measurements were made by adding weighed quantities of water and of butyric acid to dried benzene. The heat evolved per gram of powder on immersion has been plotted against the concentration of the polar liquid before adsorption. The total weight of liquid used for a determination was kept constant. It was found that a concentration of butyric acid equal to 3.7×10^{-6} moles per gram of powder increased the heat of immersion 23 percent; a concentration of 7.7×10^{-5} moles per gram of powder increased the heat of immersion practically to that for pure butyric acid. With water the effect is even greater; this is due in part to the difference in the area occupied by water and

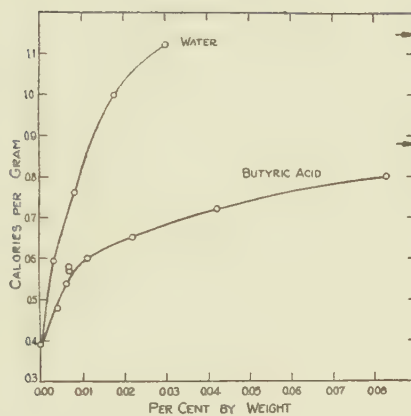


Figure 4—Energy of Immersion of Titanic Oxide in Benzene Which Contains Water or Butyric Acid.

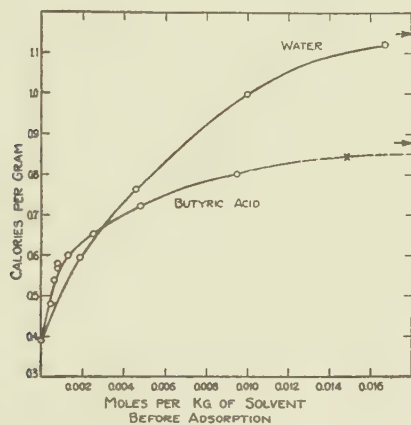


Figure 5—Energy of Immersion of Titanic Oxide in Benzene Which Contains Water or Butyric Acid.

butyric acid molecules.

The arrows to the right in Figures 4 and 5 represent the values for the heats of immersion of titanic oxide in pure water and pure butyric acid. The cross on the butyric acid curve at a concentration equal to 0.015 mol per kilogram of solvent was found to correspond to a concentration of 0.008 mol per kilogram after adsorption from direct measurements by Gans. The amount of heat developed is almost at a maximum at this point. Calculations on the basis of the area used for titanic oxide in table IV give 15.4 sq. $\text{\AA}$ for the average area occupied by a butyric acid molecule on the surface of titanic oxide.

Tables 6 and 7 contain the data as plotted in Figures 4 and 5 but they have been transformed so that the relations with respect to surface area are more apparent. It should be noted that column three gives the total number of molecules present per square centimeter and not the number adsorbed.

Table 6. Effect of Water on the Energy of Immersion of Titanic Oxide in Benzene.

Energy of immersion	Moles of acid per gram of powder	Molecules of acid per sq. cm. of surface before adsorption.
	$\times 10^{-5}$	$\times 10^{-14}$
Calories per gram	($\times 10^{-5}$)	($\times 10^{-14}$)
0.390	0.00	0.00
0.593	1.61	2.64
0.762	3.35	5.49
0.998	8.06	13.2
1.12	15.6	22.3

Table 7. Effect of Butyric Acid on the Energy of Immersion of Titanic Oxide in Benzene.

Energy of immersion	Moles of acid per gram of powder	Moles of acid per Kg. of solvent.		Molecules of acid per sq. cm. of surface before adsorption	Molecules of acid per Kg. of solvent after adsorption
		Before adsorption	After adsorption		
Calories per gram	6 ($\times 10$)	3 ($\times 10$)	3 ($\times 10$)	-14 ($\times 10$)	-14 ($\times 10$)
0.390	0.00	0.00		0.00	
0.479	3.76	0.46		0.617	
0.538	5.31	0.64		0.871	
0.579	6.39	0.81		1.05	
0.600	10.7	1.3		1.75	
0.652	21.4	2.5	0.2	3.51	3.1
0.721	43.1	4.8	1.0	7.07	5.1
0.801	77.2	9.4	5.1	12.7	5.9

That an approximately monomolecular film of water, butyric acid, an alcohol, or other similar liquid is adsorbed from its solution in a hydrocarbon oil is indicated both by the results of the last section and by direct experiments on adsorption. The fact that the presence of a hydroxyl group, a carboxyl group, or the —COOR group of an ester very greatly increases the energy of immersion above that for a hydrocarbon oil indicates that such polar or active groups are oriented toward the surface of the solid. (Figure 6)



Figure 6—Orientation of Molecules of Linoleic Acid, or Other Polar-Non-Polar Molecules, at Interface between a Hydrocarbon Oil and a Solid Oxide.

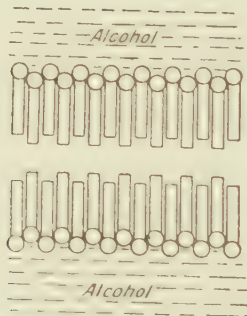


Figure 7—Orientation Where a Column of Alcohol or Acid is Broken Apart.

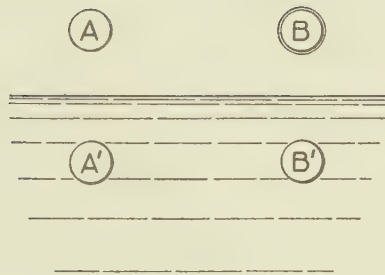


Figure 8—A-A', Immersion of a Particle Whose Surface is clean. B-B', Immersion of a Particle Whose Surface is Covered by a Film Adsorbed from Vapor of Liquid.

As has been stated, the investigations presented in this paper show that the oxides of titanium, tin, zinc, and silicon and barium sulphate act like water in attracting polar rather than non-polar groups. Thus in oils any $-\text{COONa}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{NH}$, $-\text{NHCH}_2$, $-\text{NCS}$, $-\text{COR}$, $-\text{OH}$, $-\text{SH}$, $-\text{NO}$, $-\text{CN}$, and other similar groups, orient toward the particles of oxide or sulphate and the hydrocarbon groups toward the liquid. For example, the surface of a solid oxide in contact with an alcohol orients the molecules in such a way that the hydroxyl groups are turned toward the solid and the hydrocarbon groups toward the alcohol. If the first monomolecular layer of alcohol molecules is largely oriented, it is evident that the second layer must also be oriented to some extent. Figure 7 illustrates the orientation which occurs if a column of liquid alcohol is broken apart.

The total energy of immersion is equal to the free energy, f_i , plus the latent heat of immersion, l_i , or

$$h = f_i + l_i$$

As has been stated, there is no known method for determining the extremely important free energy, f_i , which is equal to the free surface energy, γ_s of the solid, minus that of the interface, or

$$f_i = \gamma_s - \gamma_{s,l}$$

A quantity called the "adhesion tension" is now widely used. It is supposed to represent a force, t_a , which acts to cause spreading of a liquid over the surface of a solid.

If expressed in dynes per centimeter it is equal to the number of ergs which expresses a peculiar type of free energy of immersion, that is, for a surface which is already covered before immersion by an adsorbed film in equilibrium with the vapor of the liquid. It is smaller than the true free energy of immersion of the liquid and the difference between the two depends upon the vapor pressure and other factors. This difference is unknown, but the corresponding difference for the total energy has been determined for a few substances. Thus, the value for the immersion of dry titanic oxide in water is 1.15 calories, but in the presence of water vapor at 25 C. this is reduced to 0.89 calorie per square centimeter or to 77 per cent of the true value.

The relation between the true free energy of immersion and the free energy of immersion known improperly as the "adhesion tension" is exhibited more clearly in Figure 8. Here A represents a particle of solid which has a clean surface. After immersion it is represented by A'. The free energy change which occurs is designated as the "free energy of immersion." Particle B does not have a clean surface, but is covered with a film deposited from the vapor of the liquid with which the film is supposed to be in equilibrium. The decrease of surface energy which takes place when B is immersed in the liquid is also a free energy of immersion, but is much smaller than the true free energy of immersion of the solid particle. As has just been stated, the energy

change when B is immersed in the liquid is often called the "adhesion tension," but this is an incorrect term, since it represents neither a force nor an energy of adhesion and its value represents a free energy change rather than a tension. It should be called the final free energy of immersion.

The free energy of immersion, f_1 , of the powder already coated with a film (or the "adhesion tension" t_a) is equal to the true free energy of immersion, f_1 , minus the positive number which gives the magnitude of the lowering of the free surface energy, f_f , of the powder due to the presence of the film, or

$$(t_a) = f'_1 = f_1 - f_f = \gamma_s - \gamma_{s,l} + \Delta\gamma_f$$

in which $\Delta\gamma_f$ is the change in the free energy, f_f , due to the presence of the film. Numerous determinations of the "adhesion tension" have been made by Bartell¹.

Conclusions

(1) The energy relations at the interface between solid oxides or barium sulphate and organic liquids are similar to those between water and the same organic liquids, but polar groups ($-\text{OH}$, $-\text{COOH}$, $-\text{COONa}$, etc.) are much more strongly attracted by the solid oxide than by water.

(2) The energy of immersion of powdered titanic oxide, stannic oxide, zinc oxide, silica, and barium sulphate in an organic liquid is small for hydrocarbons, but is much larger if polar groups, such as $-\text{COOR}$, and especially $-\text{OH}$

1 Bartell, Ind. and Eng. Chem. 19, 1277, (1927)

or --COOH , are present. The energy in water, a polar liquid, is still higher.

(3) Extremely small quantities of water in benzene increase the energy of immersion of these solids to about three times the value for pure benzene, while a very small amount of butyric acid in the benzene may nearly double the value.

(4) These facts indicate that if the solid is immersed in butyric acid or alcohol, or in other similar organic liquids of the polar-non-polar type, the molecules of the liquid at the interface orient themselves in such a way that the polar group is toward the surface of the solid and the non-polar group toward the oil.

(5) The evidence indicates that in benzene or any other hydrocarbon oil an immersed surface of a solid becomes covered with an adsorbed mono-molecular film of water, of butyric acid, or of any similar substance, whose molecules contain a polar group, if these are present in solution. The adsorption is much greater than that at the interface between oil and water in the sense that in extremely dilute solutions which give an incomplete mono-molecular film, the amount adsorbed on unit area of the interface with the solid is much greater than that on the same area of interface between the oil and water.

(6) Titanic oxide, stannic oxide, zinc oxide, silica, and barium sulphate act in an entirely similar way with respect to their surface energy relations. The only specific difference is that the chemical action of acids is more mark-

ed with zinc oxide than with the others.

(7) Soaps are highly adsorbed from solutions in hydrocarbon oils by any of these oxides.

During the course of this work Dr. W. D. Harkins has offered many helpful suggestions for which I am deeply grateful. I also appreciate the interest and aid of Mr. W. L. Ryan and the Titanium Pigment Company.

